

MARKED ANTIOXIDATIVE ACTIVITY DEVELOPED IN ROASTED RAPESEED OILS

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ABSTRACT

Roasting of rapeseed at above 150 °C was shown to cause marked antioxidative activity in extracted oil. The activity increased with increasing roasting temperature, especially above 200 °C. Changes in browning and some minor components such as tocopherol, chlorophyll, sulfur and phosphorus were determined. Active products isolated by XAD-7 column followed by elution with ethyl acetate were investigated.

INTRODUCTION

Roasted rapeseed oil, called akamizu in Japanese, has been used for flavor and color to prepare fried tofu, a traditional and important health food in Japan. As reported in the preceding congress, we first investigated the effect of roasting rapeseed on flavor, color and other properties of the oil (1). It was shown that roasting at 140 °C for 10 to 30 min was most favorable in developing good flavor that spicy and little bitterness. There was some difference between rapeseed varieties of high erucic acid and canola in such flavor development; the former was better in characteristic roasted flavor probably due to its higher content of sulfur compounds. Roasting above 160 °C was unfavorable because of development of somewhat burned flavor. However, in the case of sesame seed, oil roasted at 180 °C or above has been widely used in Asian countries as an important cooking oil with characteristic flavor as well as high stability for oxidative deterioration (2). Therefore, it seems probable that roasting rapeseed also gives rise to higher antioxidative activity than conventional refined rapeseed oil.

This paper reports on the effects of roasting conditions on the development of antioxidative properties as well as browning and flavor of rapeseed oil and on investigations to isolate the antioxidative products in the roasted oil using various chromatographies.

EXPERIMENTAL

Material

Rapeseed of the variety "canola" (produced in Canada) was mainly used but in some experiments the variety "high erucic acid" (Hi er)(produced in Japan) was also used for comparison.

Seed Roasting and oil extraction

Roasting was done using a specially made experimental roasting apparatus equipped with a heat control system using a far infrared ray heater and a measuring and recording system of temperature of roasting material.

Oil was extracted using a hand press model extruder, and filtered by filter paper with no further purification.

Antioxidative activity

Antioxidative activity was measured mainly by weighing method and partly by rancimat method and TBA method. In the weighing method, the activity was determined by induction period (I.P.) to indicate 5% increase in weight by autoxidation during storage at 40 or 60 °C in air.

RESULTS AND DISCUSSION

Effect of roasting temperature and time on antioxidative activity

Antioxidative activity of intact roasted seed oils determined by weighing method is shown in Table 1. Development of the activity was observed even in oils roasted at 140 °C or 150 °C for 30 min but, it increased markedly at above 180 °C and gave a very stable oil by roasting at 200 °C even for as short a time as 10 min. The oils became brown almost in parallel with increase in the antioxidative activity as shown in Table 2, and showed a burned flavor with somewhat irritant and bitter taste at above 180 °C.

Table 1. Effect of roasting condition on antioxidative activity of rapeseed oil (weighing method, at 60 °C)

Roasting (°C/min)	None	140/30	150/10	150/30	180/10	200/10
Induction period (I.P.) (days)	3	15	17	15	42	70

Changes in minor components in rapeseed oil by roasting

As is well known, tocopherol homologs are very important antioxidative components in conventional vegetable oils. Changes in content of tocopherols in the roasted rapeseed oils (canola and Hi-er) by roasting at 190-200 °C for 10 min were determined by HPLC analysis. As shown in Table 2, no significant changes in tocopherol content was observed in each rapeseed oil by roasting. This suggests that the strong antioxidative activity developed in roasted oils is due to the formation of some roasted products acting directly as strong antioxidants and /or indirectly as strong synergists to tocopherols and other components.

Table 2. Tocopherol content in roasted rapeseed oil (at 190-200 °C 10 min) (Tocopherol: mg/100g oil)

Rapeseed	α -toco	β -toco	γ -toco	δ -toco	Total
roasted (canola)	26.0	0.4	81.8	1.0	109.2
roasted (Hi-er)	24.1	0.3	53.6	0.6	78.6
unroasted (canola)	21.7	0.9	51.1	1.2	74.9

Changes in other minor components and color of oil by roasting of canola rapeseed are shown in Table 3. As indicated by the degree of yellow and red in

the Lovibond chromaticity diagram, color of oil turned red brown with increase in roasting temperature and time, especially by roasting at above 190 °C. The similarity observed in the increasing curves of antioxidative activity and browning suggests that some browning products formed by roasting play an important role in developing antioxidative activity.

Content of chlorophyll was not much changed by roasting and only decreased somewhat at above 190 °C and by long heating time, e.g. 30 min. The role of chlorophyll and its degradation products in antioxidative activity is complicated, because sometimes they act as a strong prooxidant and other times as an effective antioxidant, influenced especially by light.

Sulfur content increased clearly by roasting at above 190 °C or at 170 °C for a long time, probably due to degradation of some sulfur containing compounds such as thioglucosinolates and S-containing amino acids along with increase in oil soluble sulfur compounds under such roasting conditions. On the other hand, phosphorus content decreased by roasting at higher roasting temperature, suggesting some denaturation of phospholipids to oil insoluble products. Some sulfur and phosphorus compounds in food were known to act as antioxidant, so it seems probable that the changes in sulfur and phosphorus content of the roasted oils influence the antioxidative activity, but their effects are not yet clear.

Table 3. Changes in minor components and color of rapeseed oil by roasting (canola)

Roasting °C / min	Color (Lovibond lin)	Chlorophyll (ppm)	Sulfur (ppm)	Phosphorus (ppm)
150 / 10	Y 50 / 3.2 R	10.32	94.3	373
150 / 60	Y 60 / 5.2 R	10.33	137.1	462
160 / 10	Y 50 / 4.5 R	10.69	119.3	478
160 / 45	Y 70 / 5.5 R	9.50	183.6	410
170 / 10	Y 70 / 4.8 R	10.64	199.5	457
170 / 30	Y 70 / 7.5 R	8.65	348.1	353
190 / 10	Y 79 / 7.0 R	9.06	363.1	342
200 / 5	Y 79 / 11.0 R	7.09	503.3	119

Isolation of antioxidative products by column chromatography

Isolation of antioxidative products in the roasted seed oil was investigated using various adsorbents. Active carbon powder showed strong adsorption capacity of the antioxidative activity as well as brown color but very poor elution of the activity by organic solvents. Acid clay was weak in adsorption both of activity and color. Amberlite XAD-7 was effective in adsorption of the brown products though not so strong as active carbon but in this case the adsorbed activity and browning products could be eluted mostly with ethyl acetate and methanol. The rapeseed oil roasted at 220°C was then chromatographed on XAD-7 column with n-hexane, and the adsorbed brown products were eluted with ethyl acetate followed by methanol. Further purification, antioxidative activity and chemical properties are being investigated.

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